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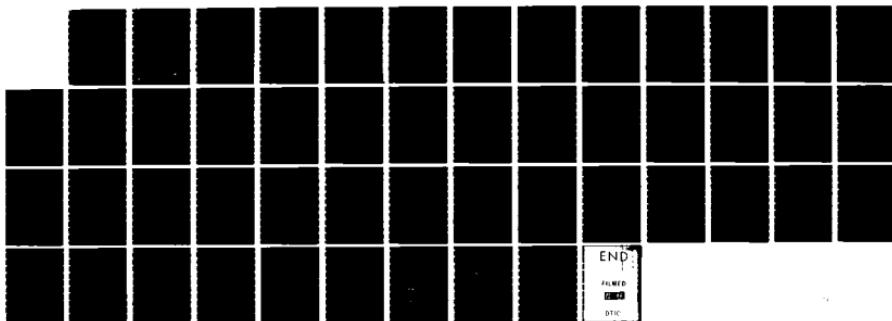
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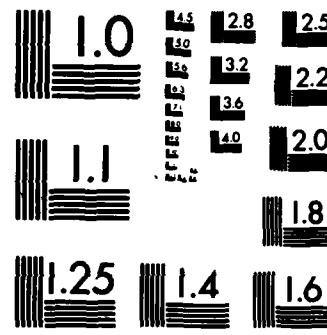
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IONIC REACTIONS OF ATMOSPHERIC IMPORTANCE

BY

DAVID SMITH and NIGEL G. ADAMS

DEPARTMENT OF SPACE RESEARCH

UNIVERSITY OF BIRMINGHAM

BIRMINGHAM B15 2TT

ENGLAND

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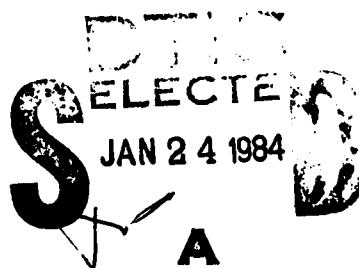
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20. Abstract A variable-temperature flowing afterglow/Langmuir probe (FALP) apparatus has been used to study the temperature dependence of a number of electron-ion dissociative recombination coefficients, α_e , and electron attachment coefficients, β , over the temperature range 200-600 K. Thus $\alpha_e(O_2^+)$, $\alpha_e(NO^+)$ and $\alpha_e(NH_4^+)$ have been shown to vary inversely with temperature, T, as $\alpha_e \propto T^n$ with $n = 0.7, 0.9$ and 0.6 respectively. $\alpha_e(H_3O^+)$ was found to be independent of temperature. $\beta(CCl_4^+)$, $\beta(CCl_3F)$ and $\beta(SF_6^+)$ were all very large, close to their theoretical maximum values ($\sim 4 \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ at 300 K) and varied only very slowly with temperature over the available range, whereas $\beta(CCl_2F_2^+)$, $\beta(CHCl_3^+)$ and $\beta(Cl_2^+)$ were smaller and increased appreciably with temperature. From the data, activation energies, E_a , were obtained for the dissociative attachment reactions of CCl_4^+F , $CCl_3^+F_2$, $CHCl_3^+Cl$, and Cl_2^+ . Thus $E_a(CCl_4^+F) = 0.02 \text{ eV}$, $E_a(CCl_3^+F_2) = 0.15 \text{ eV}$, $E_a(CHCl_3^+Cl) = 0.12 \text{ eV}$ and $E_a(Cl_2^+) = 0.05 \text{ eV}$		

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PREFACE

This work is part of a larger programme of ionic reaction studies at thermal energies conducted by the authors of this report. The overall programme includes studies of ion-molecule reactions, ion-ion recombination, electron-ion recombination, electron attachment and other plasma reaction processes. The work is largely intended as a contribution to the physics and chemistry of natural plasmas such as the ionosphere and the interstellar medium and of laboratory plasma media such as gas laser systems. A great deal of relevant data has been obtained principally by exploiting the versatile Selected Ion Flow Tube (SIFT) and the Flowing Afterglow/Langmuir Probe (FALP) techniques which were developed in our laboratory. Part of the overall programme is also supported by a grant from the Science and Engineering Research Council.

A major contribution to the work described in this report has been made by Dr. Erich Alge.

I INTRODUCTION

Our major commitment under the terms of the grant is to study a range of ionic processes which occur in low temperature plasmas such as the Earth's ionosphere, including ion-ion recombination, electron-ion recombination and electron attachment. Such studies are possible using the flowing afterglow/Langmuir probe (FALP) apparatus developed in our laboratory. Previously using the FALP, we have made a detailed study of ion-ion recombination reactions with special reference to reactions which are thought to be important ionization loss mechanisms in the stratosphere and the troposphere and these data have been reported in detail in previous reports and research papers. The major effort during the last 20 months (the period with which this report is largely concerned) has been directed towards studies of electron-ion dissociative recombination and electron attachment. Thus we have determined dissociative recombination coefficients, α_e , for reactions involving some atmospheric positive ions and electron attachment coefficients, β , for several very efficient electron scavengers, including some Freons which are known to be amongst the many stratospheric pollutants. Detailed results are presented and discussed in two recent research papers which are included as Appendices to this report. The following is a brief summary of the results.

II SUMMARY OF RESULTS

(i) Dissociative Electron-Ion Recombination.

(a) O_2^+ + e: This is the most studied recombination reaction of all and was chosen for this very reason as the first reaction to study. The data obtained are in excellent agreement with previous data both in the magnitude of $\alpha_e(O_2^+)$ at 300 K and in the temperature dependence ($\alpha_e(O_2) \propto T^{-0.7}$) over the temperature range 200-600 K. Very recently we have extended the measurement of $\alpha_e(O_2^+)$ down to 95 K and a value of $4.8 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ was obtained, which indicates that the $T^{-0.7}$ power law describes $\alpha_e(O_2^+)$ over the wider temperature range of 95-600 K.

(b) $NO^+ + e$: Although the 300 K value of $\alpha_e(NO^+)$ was not seriously in doubt, the temperature dependence of $\alpha_e(NO^+)$ has been

the subject of controversy for several years (see Appendix 1). We therefore chose to study this reaction to try to establish unequivocally the temperature dependence of $\alpha_e(\text{NO}^+)$. Our data clearly indicate that $\alpha_e(\text{NO}^+) \sim T^{-0.9}$ over the range 200-600 K and is therefore consistent with data derived from ion trap experiments and with data derived from in situ ionospheric satellite data. We therefore believe that the $\alpha_e(\text{NO}^+)$ controversy has been resolved.

(c) $\text{NH}_4^+ + e$: This is a fast recombination reaction; $\alpha_e(\text{NH}_4^+)$ is determined in the present FALP experiment to be $1.35 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}$ at 295 K, which is in good agreement with previous afterglow data. $\alpha_e(\text{NH}_4^+)$ is found to vary as $T^{-0.6}$. In the course of these studies, cluster ions of the type $\text{NH}_4^+ \cdot (\text{NH}_3)_{2,3}$ could be readily generated in the afterglows by increasing the concentration of NH_3 and so $\alpha_e(\text{NH}_4^+ \cdot (\text{NH}_3)_{2,3})$ was also determined. A large value of $2.8 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}$ was obtained which is in excellent agreement with a previous stationary afterglow measurement.

(d) $\text{H}_3\text{O}^+ + e$: The result of these studies was that $\alpha_e(\text{H}_3\text{O}^+)$ was sensibly independent of temperature within the restricted temperature range (300-600 K) over which measurements could be made. However, $\alpha_e(\text{H}_3\text{O}^+)$ is quite large ($\sim 1.0 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}$) and it is not without precedence that efficient recombination reactions are not very temperature sensitive as, for example, the recombination reactions of water cluster ions, $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ (see M.T.Leu, M.A. Biondi and R.Johnsen, Phys. Rev. A7, (1973) 292).

Details of the studies of $\alpha_e(\text{O}_2^+)$, $\alpha_e(\text{NO}^+)$ and $\alpha_e(\text{NH}_4^+)$ and a comprehensive reference list are given in Appendix 1. The data for $\alpha_e(\text{H}_3\text{O}^+)$ is as yet unpublished.

(ii) Electron Attachment

For the initial studies of this interesting class of reactions we chose several reactions which were known to be fast, i.e. electron reactions with SF_6 , CCl_4 and CCl_3F , and two reactions for which previous data had indicated that the β were very temperature dependent, i.e. the CCl_2F_2 and CHCl_3 reactions. We also studied the Cl_2 reaction for which the several previous studies had resulted in seriously conflicting values of β . Indeed, the major objective of these attachment studies was to

provide accurate values of β and their temperature dependences to clarify the unusual large uncertainties surrounding the attachment coefficients for many reactions reported in the published literature.

The detailed results of this study together with an appraisal and discussion of them is given in Appendix 2. It is sufficient here to note the following. $\beta(\text{CCl}_4)$ is large and reduces slowly with increasing temperature from the 205 K value of $4.1 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$, as is also indicated by previous data. $\beta(\text{CCl}_3\text{F})$ is also large but increases slowly with temperature from the 205 K value of $2.2 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ towards the theoretical maximum value. A small activation energy, E_a , of ≈ 0.02 eV is indicated for this reaction. $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$ are about two order of magnitude smaller than the theoretical maximum value at 300 K, but increase rapidly with temperature and activation energies of $E_a(\text{CCl}_2\text{F}_2) \approx 0.15$ eV and $E_a(\text{CHCl}_3) \approx 0.12$ eV are obtained. $\beta(\text{Cl}_2)$ is relatively small at 300 K ($2 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$) and increases slowly with temperature, indicating an $E_a(\text{Cl}_2) \approx 0.05$ eV. In all these five reactions, Cl^- was the only product ion observed. $\beta(\text{SF}_6)$ is measured to be $3.1 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ at 300 K which is a little larger than previous experiments have indicated. A significantly larger value is obtained at 450 K in our experiment suggesting a peak in $\beta(\text{SF}_6)$ near this temperature. SF_6^- is the only product ion at 300 K, but SF_5^- becomes an increasingly important product with increasing temperature.

III CONCLUSIONS

The results of the FALP studies of dissociative recombination and electron attachment described in this report clearly demonstrate the value of the FALP technique for studies of a wide variety of plasma reaction processes. The data obtained relating to these processes and also the data obtained previously for ion-ion recombination have found important applications in aeronomy and laser physics. Very much more can be achieved with the FALP apparatus and it is hoped to greatly increase the number of reactions studied in each category in order to provide further critical data for aeronomy, laser devices and other applications.

APPENDIX 1

MEASUREMENTS OF THE DISSOCIATIVE RECOMBINATION

COEFFICIENTS OF O_2^+ , NO^+ AND NH_4^+ IN

THE TEMPERATURE RANGE 200-600 K

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Measurements of the dissociative recombination coefficients of O_2^+ , NO^+ and NH_4^+ in the temperature range 200-600 K

E Alge, N G Adams and D Smith

Department of Space Research, University of Birmingham, Birmingham B15 2TT, England

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Abstract. Measurements are presented for α_i , the dissociative recombination coefficients with electrons of O_2^+ , NH_4^+ and NO^+ under truly thermalised conditions within the temperature range 200-600 K, using a flowing afterglow/Langmuir probe apparatus. $\alpha_i(O_2^+)$ is found to vary as $\sim T^{-0.7}$ in close accord with previous pulsed afterglow data for $\alpha_e(O_2^+)$ and $\alpha_i(O_2^+)$ and with values for $\alpha_e(O_2^+)$ inferred from ion trap data. $\alpha_i(NH_4^+)$ is found to vary as $\sim T^{-0.6}$. $\alpha_i(NO^+)$ is found to vary as $\sim T^{-0.9}$ which is reasonably consistent with previous pulsed afterglow data for $\alpha_e(NO^+)$. These data are also compared with values of $\alpha_e(NO^+)$ measured in a pulsed afterglow experiment and those derived from ion trap and merged beam cross section data and from atmospheric observations.

1. Introduction

Dissociative recombination reactions of molecular positive ions with electrons have been studied for many years because they represent an important process of loss of ionisation both in laboratory plasmas such as gaseous lasers (Biondi 1976) and in naturally occurring plasmas such as the ionosphere and the interstellar gas clouds (see the reviews by Smith and Adams 1980, 1981). The primary objective of most studies has been to determine the recombination coefficients, α , for particular positive ion species and the way they vary either with the electron temperature T_e when $T_e > T_i$, T_g , denoted in this paper as α_e , or under thermal equilibrium conditions such that $T_e = T_i = T_g$ (the electron, ion and gas temperatures respectively), denoted as α_i . Notable amongst the many techniques used for these studies are the pulsed (time-resolved) afterglow technique (Frommhold *et al* 1968, Weller and Biondi 1968) for determining α_i and α_e , and the ion trap technique (Walls and Dunn 1974, Heppner *et al* 1976) and merged-beam technique (Auerbach *et al* 1977, Mull and McGowan 1979) for measuring the variation of the recombination cross section, σ_E , with electron energy.

In this paper we report the results obtained for α_i for the following reactions:



Reactions (1) and (2) are of great significance in the ionosphere but while good

agreement exists between the data obtained with various techniques for reaction (1) that for reaction (2) is still disputed.

We have obtained these data using a new variable-temperature flowing afterglow/Langmuir probe (FALP) apparatus, similar to that previously used to determine positive-ion-negative-ion neutralisation rate coefficients at thermal energies (see the review by Smith and Adams 1983).

2. Experimental

The FALP technique has been described in detail in previous papers (Smith *et al* 1975, Smith and Church 1976, Smith and Adams 1983) and so it is only necessary to outline its general features and to highlight those modifications to the apparatus which were required before the rapid process of dissociative recombination could be studied accurately. The essential elements of the apparatus are illustrated in figure 1(a). A carrier gas, usually helium, is introduced into a stainless-steel flow tube approximately 1 m long and 8 cm in diameter and is constrained to flow down this tube by the action of a Roots pump. Ionisation is created in a microwave discharge upstream in the carrier gas and an afterglow plasma containing He^+ , electrons and He^m is distributed along the length of the flow tube. Typical carrier gas pressures ranged from 0.6 to 1.0 Torr and the electron densities, n_e , established in the afterglow plasma could be varied up to a maximum of about $7 \times 10^{10} \text{ cm}^{-3}$. The absolute electron (and ion) densities and the electron temperature can be measured at any point along the axis

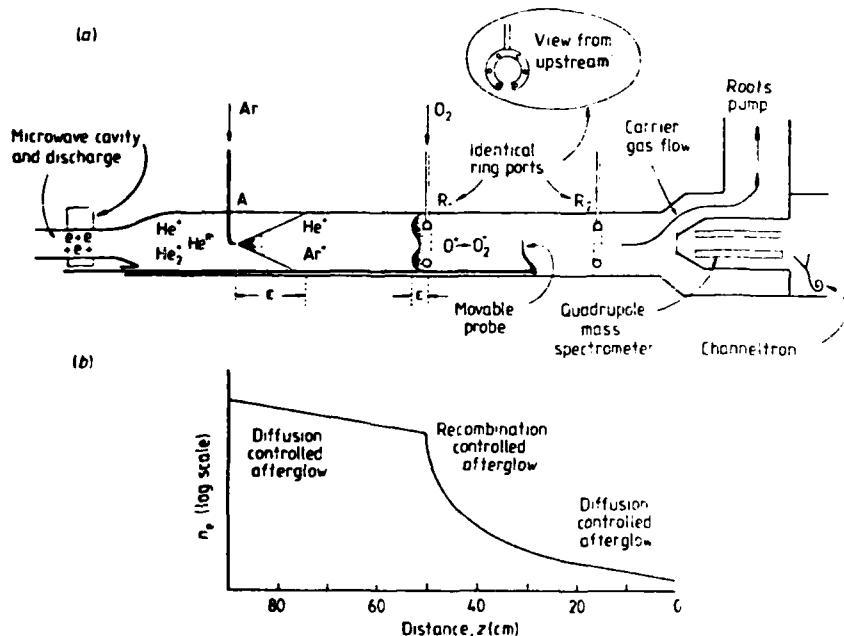


Figure 1. (a) Schematic representation of the FALP experiment, including details of the gas inlet ports, diagnostic instruments, etc. (b) Typical electron density profile along the flow tube during dissociative recombination studies.

of the flow tube using a movable Langmuir probe (see e.g. Smith and Plumb 1972, Smith *et al* 1975).

Argon is introduced through the axial port A (see figure 1(a)) to destroy the He^m thus eliminating a source of ionisation in the afterglow. Also any He_2^+ formed in three-body reactions between He^+ and He will be rapidly converted to Ar^+ . The reactant molecular ions are formed by the addition of a suitable gas via either of the 'ring ports' R_1 or R_2 . These ring ports were designed to minimise the mixing length, ϵ , (often termed the 'end correction' in flow tube experiments) which, for an axial port such as A, is too extensive for dissociative recombination studies (see figure 1(a)). R_1 and R_2 consist of 2 mm diameter stainless-steel tubing in the form of a ring of diameter 3 cm positioned symmetrically about the axis of the flow tube. A series of small holes (diameter 0.5 mm) drilled in the upstream-facing part of the ring direct the effusing reactant gas against the carrier gas flow. This simple procedure reduces ϵ to about 1 to 2 cm depending on the flow rates of the reactant and the carrier gases (for an axial port such as A, $\epsilon \approx 10$ cm). The extent of ϵ can be estimated visually by observing the light emitted from the afterglow following the addition of reactant gas and by inspection of the reciprocal electron density plots (see figure 2(b)). Changes in the ion compositions of the plasmas (both positive and negative ions) were continuously monitored by the downstream quadrupole mass spectrometer/ion detection system.

Prior to the addition of the reactant gas the only loss process for ionisation downstream of port A is due to ambipolar diffusion of He^+ and Ar^+ ions with electrons. This is always the situation between ports A and R_1 and, at the pressures of the experiments, results in a slow exponential decrease in n_e with distance, z , along the flow tube as is illustrated in figure 1(b) (all z distances are referenced to the downstream mass spectrometric sampling orifice). The addition of molecular gas into R_1 initiates a sequence of ion-molecule reactions which generate a terminating molecular ion species. This, at suitably high n_e (and n_+ , the molecular positive ion density), then results in a more rapid decrease of n_e with z due to the onset of recombination (figures 1(b) and 2(a)). Thus the afterglow plasma becomes recombination controlled in this region but further downstream where n_e has decreased to sufficiently small values, the plasma will again become diffusion controlled as illustrated. By measuring n_e as a function of z coupled with a measurement of the plasma flow velocity, v_p , (which is typically 10^4 cm s $^{-1}$ and is measured by pulse modulating the microwave discharge—see Adams *et al* 1975), both diffusion coefficients and recombination coefficients can be determined separately. When both ambipolar diffusion and recombination are occurring simultaneously in the plasma, the appropriate continuity equation for n_e is:

$$v_p \frac{\partial n_e}{\partial z} = D_a \nabla^2 n_e - \alpha_i n_+ n_e \quad (4)$$

where D_a is the ambipolar diffusion coefficient. To determine α_i it is desirable to ensure that recombination is the only significant loss process. This can be accomplished by operating at high helium pressure (to diminish diffusive loss) and at high n_e (to enhance recombination loss). Under these conditions the diffusion term in equation (4) can be neglected and the solution to the continuity equation becomes:

$$\frac{1}{n_e(z_1)} - \frac{1}{n_e(z_2)} = \frac{\alpha_i}{v_p} (z_2 - z_1) \quad (5)$$

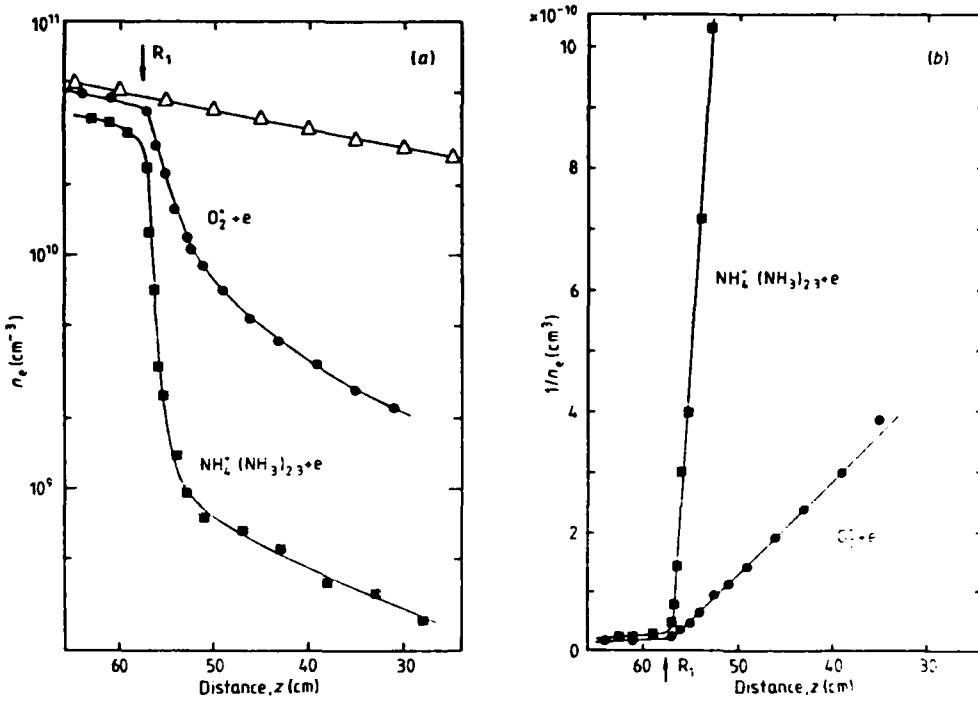


Figure 2. Electron density profiles (a) and the corresponding reciprocal density ($1/n_e$) plots (b) obtained at a helium pressure of 0.6 Torr and a temperature of 295 K. (a) Δ , diffusion controlled afterglow plasma (He^+ , Ar^+ , electrons), i.e. no reactant gas has been added. Upon addition of sufficient reactant gas through port R_1 (see figure 1(a)) the afterglow plasma becomes recombination controlled (full symbols): \bullet , plasma containing only O_2^+ ions; \blacksquare , plasma containing both $\text{NH}_4^+(\text{NH}_3)_2$ and $\text{NH}_4^+(\text{NH}_3)_3$ ions. (b) The reciprocal electron density plots corresponding to the recombination controlled profiles of (a).

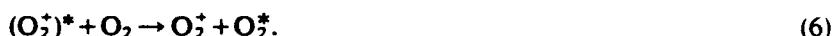
A plot of $1/n_e(z)$ against z then provides a value for α_1 . As examples, plots of n_e against z are given in figure 2(a) for the relatively slowly recombining O_2^+ ions and for the rapidly recombining $\text{NH}_4^+(\text{NH}_3)_{2,3}$ cluster ions. Note the increase in the gradient of n_e immediately downstream of the port R_1 , especially for the cluster ion reaction. This indicates that α_1 for this reaction is larger than that for the O_2^+ reaction. When n_e becomes sufficiently small the plasma will become diffusion controlled again as is best demonstrated by the cluster ion curve in figure 2(a). These data are replotted in figure 2(b) as $1/n_e$ against z and the linearity of these plots is a clear indicator of loss of ionisation by recombination. It should be appreciated that for these plots to be taken as evidence for a recombination controlled plasma they should be linear over at least two factors of two ($\times 4$) and preferably three factors of two ($\times 8$) change in n_e (Gray and Kerr 1962). As can be seen in figure 2(b) these data (as do all the data obtained in this study) satisfy this criterion. Note also the very rapid conversion from a diffusion dominated plasma upstream of R_1 to a recombination dominated plasma downstream which indicates a small ϵ (and shows the value of the new port design).

The FALP technique can be used to determine the recombination coefficient for any positive ion which can rapidly be established as the only recombining species in the plasma (as determined using the mass spectrometer). However great care must

be exercised when interpreting mass spectra obtained from a recombining plasma since the recombination process preferentially removes rapidly recombining ions. Thus atomic ions, which do not recombine with electrons at an appreciable rate, may often be dominant components in the downstream region of the plasma even though they are not the most important components of the plasma in the upstream region. To account for this potential problem, port R_2 was specifically included in the apparatus and sited much closer to the mass spectrometer sampling orifice. Thus the reactant gas could be routed between R_1 and R_2 in order to investigate changes in the ion composition of the plasma with z . Also as a routine procedure when determining the identity of the recombining ions, n_e was reduced to values at which dissociative recombination was negligible.

The FALP apparatus can be operated between the temperature limits 80 to 600 K by the use of refrigerant liquids or ohmic heaters. Most of the data reported here were obtained over the range 200 to 600 K, since at lower temperatures ion clustering reactions occurred rapidly (e.g. generating $O_2^+O_2$, NO^+NO etc). The experiments were conducted under conditions such that $T_e = T_s = T_g = T$ and thus α_e was obtained for each reaction studied. The removal of the He^m and the addition of the molecular reactant gas ensured that the electrons were thermalised at the gas temperature. This we have established from previous detailed studies of electron temperature relaxation rates in a FALP apparatus (Dean *et al* 1974) by exploiting the Langmuir probe to determine T_e .

We confidently expect the reactant ions in these experiments to be in their ground electronic and equilibrium vibrational/rotational states at each particular gas temperature (which was measured by calibrated thermocouples immersed in the gas). This we believe to be so because, although the molecular ions on production are almost certainly excited, they will undergo resonance charge or proton transfer with their parent molecules which is known to quench both electronic and vibrational excitation effectively (see Albritton 1979, Lindinger *et al* 1981), as for example:



Rotational relaxation is ensured by the high collision frequency of the molecular ions with the ambient helium atoms.

The absolute values of the measured recombination coefficients are estimated to be subject to an uncertainty of not more than $\pm 15\%$. The main contribution to this error figure arises from the uncertainty in the current collecting area of the probe which is reflected directly in the n_e values ($\leq 10\%$). Smaller contributions are due to inaccuracies in the measured plasma velocity and in the derived best fit slopes of the $1/n_e$ against z plots. Since the uncertainty in the probe area represents a systematic error then the relative values of α , are subject to an error of not more than $\pm 10\%$.

3. Results

3.1. $O_i^+ + e$

The O_2^+ ions were created by adding O_2 into the afterglow via port R_1 , thus initiating the reactions:



The O_2 was added in sufficient concentration ($\sim 5 \times 10^{14}$ molecules/cm 3) to ensure that these reactions completely converted the He^+ and Ar^+ into O_2^+ in a distance of about 1 to 2 cm along the flow tube, but insufficient to convert the O_2^+ ions to $O_2^+O_2$ cluster ions via three-body association (Adams *et al* 1970, Good 1975). Association reactions become increasingly rapid with decreasing temperature and therefore ion clustering is potentially troublesome at low temperatures (see below). $\alpha_e(O_2^+)$ was determined at temperatures of 205, 295, 420, 530 and 590 K from reciprocal density plots of the kind shown in figure 2(b) and the values obtained are presented in the log-log plot in figure 3. Over this temperature range $\alpha_e(O_2^+)$ conforms approximately to a power law of the form:

$$\alpha_e(O_2^+) = 1.95 \times 10^{-7} \left(\frac{300}{T} \right)^{0.7} \text{ cm}^3 \text{ s}^{-1}. \quad (8)$$

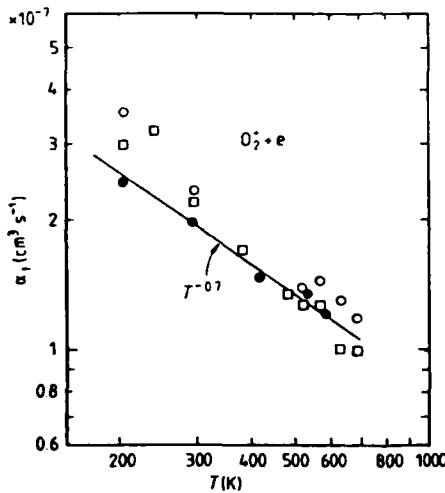


Figure 3. Temperature dependence of the recombination coefficient $\alpha_e(O_2^+)$ (see text). The line is drawn through the present FALP values (●). The various data of Kasner and Biondi (1968) are indicated as: ○, obtained in Ne/O_2 mixtures; □, obtained in $Ne/Kr/O_2$ mixtures.

Also included in figure 3 are the data obtained by Kasner and Biondi (1968) using the pulsed afterglow technique and it can be seen that the data from the two experiments are in good agreement above 300 K and indicate essentially the same temperature variation. However, at lower temperatures the pulsed afterglow values are somewhat larger than the present value which may be a manifestation of ion clustering in the higher pressure pulsed afterglow experiment (Biondi and co-workers have shown that cluster ions, including $O_2^+O_2$, generally have larger recombination coefficients, see e.g. Biondi 1973—see also below). A dependence of order $T_e^{-0.7}$ for $\alpha_e(O_2^+)$ was also obtained in the pulsed afterglow experiment of Mehr and Biondi (1969). Walls and Dunn (1974) using their ion trap technique obtained relative values of $\sigma_E(O_2^+)$ down to electron energies of 0.2 eV. The best fit line to their data indicated an $E^{-1.16}$ variation for σ_E at the lowest energies (which approximates to an α_e variation of $\sim T^{-0.66}$) which is in good agreement with the afterglow results. Data obtained by Mul and McGowan (1979) for $\sigma_E(O_2^+)$ using the merged beam technique agree within

error with the ion trap data but indicate a E^{-1} variation, i.e. a somewhat weaker temperature dependence for $\alpha_e(O_2^+)$ ($\sim T^{-0.5}$). Thus the variation with temperature of both $\alpha_e(O_2^+)$ and $\alpha_e(NH_4^+)$ are quite similar, the bulk of the data indicating a common dependence proportional to $T^{-0.7}$ at low temperatures. The $\alpha_e(O_2^+)$ temperature dependence becomes slightly weaker at higher temperatures (Mehr and Biondi 1969, Torr and Torr 1978, Mul and McGowan 1979).

Theoretical descriptions of dissociative recombination distinguish between a 'direct' process and an 'indirect' process (see the review by Bardsley and Biondi 1970). For the direct process, in which the electron is envisaged to be captured directly into a repulsive state of the neutral molecule, α_e (and α_i) is predicted to vary as $T_e^{-0.5}$ at the low temperatures of the present experiment. The indirect process is envisaged to proceed via a vibrationally excited Rydberg level of the neutral molecule from which predissociation occurs and then α_e is predicted to vary as $T_e^{-1.5}$. The combined experimental results for O_2^+ indicate that the direct process is favoured in the low-temperature regime but with some small contribution due to the indirect process.

3.2. $NH_4^+ + e$

The NH_4^+ ions were created by adding ammonia, NH_3 , to the afterglow plasma via port R, thus initiating the following reaction sequences:



For these studies, sufficient NH_3 was added to produce the NH_4^+ ions rapidly but insufficient to generate ion clusters of the kind $NH_4^+.(NH_3)_n$. In associated experiments these cluster ions were deliberately produced (see below). $\alpha_i(NH_4^+)$ was determined at temperatures of 295, 415, 460, 540 and 600 K and the values obtained are plotted as a function of temperature in figure 4. Note that $\alpha_i(NH_4^+)$ is typically about an order

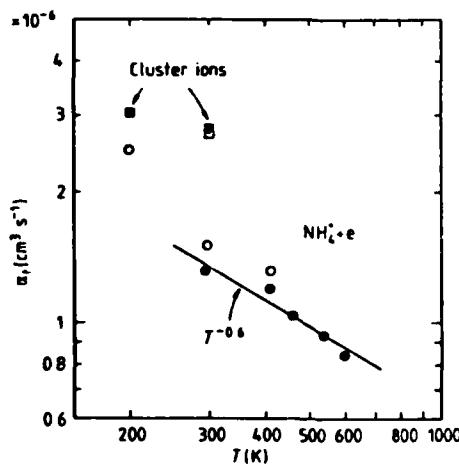


Figure 4. Temperature dependence of the recombination coefficient $\alpha_i(NH_4^+)$ (see text). The line is drawn through the present results (●). The data of Huang *et al.* (1976) for $\alpha_i(NH_4^+)$ are indicated by O. Also included are recombination coefficients for cluster ions: □, $NH_4^+.(NH_3)_2$; ■, $NH_4^+.(NH_3)_3$ due to Huang *et al.* (1976); ▽, present results for a mixture of $NH_4^+.(NH_3)_2$ and $NH_4^+.(NH_3)_3$.

of magnitude greater than $\alpha_i(O_2^+)$. No measurements were made at 200 K in our experiments since at this lower temperature ion clustering prevented the creation of a plasma containing only NH_4^+ and electrons. $\alpha_i(NH_4^+)$ over this more limited temperature range can approximately be described by the power law:

$$\alpha_i(NH_4^+) = 1.35 \times 10^{-6} \left(\frac{300}{T}\right)^{0.6} \text{ cm}^3 \text{ s}^{-1}. \quad (10)$$

This $T^{-0.6}$ dependence implies that the direct recombination process is dominant in this reaction. Also included in figure 4 are the pulsed afterglow data of Huang *et al* (1976); note the good agreement between these data and the present data at about 300 and 400 K. However the pulsed afterglow value at about 200 K is somewhat larger than that based on a $T^{-0.6}$ variation; this could be due to insufficient correction to the data to account for the presence in these experiments of the more rapidly recombining cluster ions. In a subsidiary experiment at 300 K we were able to establish an equilibrium concentration ratio of $NH_4^+.(NH_3)_2$ and $NH_4^+.(NH_3)_3$ ions in the afterglow by adding excess NH_3 . Recombination proceeded even more rapidly than for NH_4^+ ions and a composite α_i for the recombination of these cluster ions of $2.8 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ was obtained, the largest value obtained to date for any reaction studied in our experiments. This value is in excellent agreement with that obtained by Huang *et al* for $NH_4^+.(NH_3)_2$ cluster ions at 300 K and very similar to that for $NH_4^+.(NH_3)_3$ cluster ions at 200 K (see figure 4).

The NH_4^+ reaction has also been studied in the ion trap experiment by DuBois *et al* (1978). To convert the $\sigma_E(NH_4^+)$ data to α_e values, assumptions had to be made on the form of σ_E at near-thermal energies. The uncertainty in the form of $\sigma_E(NH_4^+)$ at low energies makes it hazardous to estimate $\alpha_e(NH_4^+)$ from these data. However based on a $T^{-0.6}$ variation of $\alpha_e(NH_4^+)$, the absolute magnitudes of the estimated $\alpha_e(NH_4^+)$ values in the thermal energy range are about a factor 2 smaller than the afterglow values.

3.3. $NO^+ + e$

The NO^+ ions were created by adding nitric oxide, NO, to the afterglow initiating the reactions:



It is known that the $Ar^+ + NO$ reaction generates NO^+ in the metastable $a^3\Sigma^+$ state (Dotan *et al* 1979), but the excess NO present in the plasma ensures that the NO^+ is rapidly quenched to the vibronic ground state via charge exchange with NO (see § 2). Formation of the cluster ions $NO^+ . NO$ (which most readily occurs at the lower temperatures) was prevented by limiting the amount of NO introduced into the plasma. Also it was necessary to condense out traces of nitric acid, HNO_3 , from the NO before it was introduced into the plasma, since its presence would result in the loss of electrons in attachment reactions to form negative ions and would therefore distort the dissociative recombination data. It was confirmed mass spectrometrically that attachment was not occurring. $\alpha_i(NO^+)$ was determined at 205, 295, 465 and 590 K and the values obtained are presented in figure 5. It can be seen that the variation

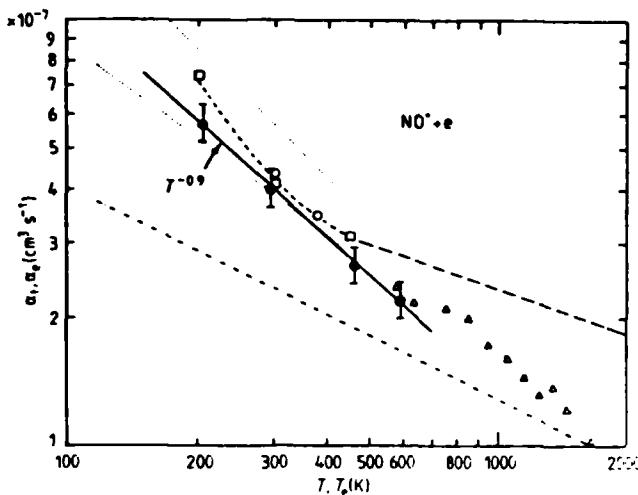


Figure 5. Temperature dependences of $\alpha_i(NO^+)$ and $\alpha_e(NO^+)$. Directly measured rate coefficients, $\alpha_i(NO^+)$: ●, present results, with error bars, joined by full line. □, Weller and Biondi (1968) and ○, Huang *et al* (1975) joined by short dashes. $\alpha_e(NO^+)$: ---, Huang *et al* (1975), measured at $T_e = T_g = 380$ K. Derived rate coefficients, $\alpha_e(NO^+)$: from Walls and Dunn (1974), using $\sigma_E(NO^+)$ data and assuming two different forms of $\sigma_E(NO^+)$ at low energies—see text; - - - - , from Mul and McGowan (1979), using $\sigma_E(NO^+)$ data obtained at low energies at which the energy scale is subject to larger errors; Δ, Torr *et al* (1977), from satellite data.

of $\alpha_i(NO^+)$ over this temperature range can be described by the power law:

$$\alpha_i(NO^+) = 4.0 \times 10^{-7} \left(\frac{300}{T} \right)^{0.9} \text{ cm}^3 \text{ s}^{-1}. \quad (12)$$

Also included in figure 5 are the pulsed afterglow values for $\alpha_i(NO^+)$ measured by Weller and Biondi (1968), and for both $\alpha_i(NO^+)$ and $\alpha_e(NO^+)$ measured by Huang *et al* (1975). These $\alpha_i(NO^+)$ data are in agreement with our data within the error limits of the experiments, except perhaps again for the lowest temperature at which, in the higher pressure pulsed afterglow experiments, effects due to clustering would be most significant. It was confirmed mass spectrometrically that cluster ions were not present in our NO^+ /electron flowing afterglow plasmas. The data of Huang *et al* (1975) indicate that $\alpha_e(NO^+)$ departs from the power law appropriate to $\alpha_i(NO^+)$ to a less rapid variation ($\sim T_e^{-0.37}$) at elevated T_e . It is clear that the value of $\alpha_i(NO^+)$ determined in our experiment at 590 K is significantly smaller than the corresponding value of $\alpha_e(NO^+)$ at $T_e = 590$ K and it is unfortunate that our experiment cannot be operated at higher temperatures to check if this divergence of $\alpha_i(NO^+)$ and $\alpha_e(NO^+)$ is maintained at higher temperatures.

Values of $\alpha_e(NO^+)$ have been derived by Walls and Dunn (1974) from their $\sigma_E(NO^+)$ ion trap data extrapolated on the basis of two different energy variations of σ_E , i.e. according to $\sigma_E \sim E^{-1.5}$, and to $\sigma_E \sim E^{-1.5}$ changing to E^{-1} below 0.01 eV. Mul and McGowan (1979) have also determined $\sigma_E(NO^+)$ using the merged beam technique and have obtained a $\sigma_E \sim E^{-1}$ dependence within the centre-of-mass electron energy range 0.009 to 0.1 eV. Thus they also derived $\alpha_e(NO^+)$ and these values together with the ion trap data are reproduced in figure 5. Since the $\sigma_E(NO^+)$ from the two

experiments are in close accord in the overlapping energy range (≥ 0.05 eV) then the differences in the derived $\alpha_e(\text{NO}^+)$ must be due to the energy dependence for $\sigma_E(\text{NO}^+)$ used at lower energies to calculate $\alpha_e(\text{NO}^+)$ at low temperatures. The form of σ_E at low energies is not readily determined because of the difficulty in accurately defining the centre-of-mass energies below 0.1 eV in ion beam experiments (e.g. see Froelich *et al* 1983). Thus larger inaccuracies are inevitably introduced into calculations of α_e at low temperatures.

As can be seen from figure 5, these derived $\alpha_e(\text{NO}^+)$ values encompass the measured $\alpha_e(\text{NO}^+)$ values but clearly the extremes of $\alpha_e(\text{NO}^+)$ are outside the errors in the present values of $\alpha_e(\text{NO}^+)$. Therefore when α_e values are required it is best to measure them directly, as was accomplished in the afterglow experiments, rather than to infer them from cross section data. Notwithstanding this comment, figure 5 shows that at the highest temperatures, the present afterglow data, the ion trap data and the merged beam data converge towards common values for $\alpha_e(\text{NO}^+)$ and $\alpha_e(\text{NO}^-)$. Also in agreement with these data are the values of $\alpha_e(\text{NO}^+)$ derived by Torr *et al* (1977) from ionospheric observations. Note that the absolute values of $\alpha_e(\text{NO}^+)$ at about 600 K determined in our experiment are in very good agreement with those derived from the ionosphere data. This is to be expected if the ions in the ionosphere are largely in their ground electronic and vibrational states which, although not positively proved, is a reasonable assumption in view of the short lifetime of vibrationally excited NO^+ in the ionosphere (Torr and Torr 1978). Torr *et al* (1977) give a best fit to their data as:

$$\alpha_e(\text{NO}^+) = 4.2 \times 10^{-7} \left(\frac{300}{T_e} \right)^{0.85} \text{ cm}^3 \text{ s}^{-1} \quad (13)$$

which is remarkably similar to our results for $\alpha_e(\text{NO}^+)$.

On balance then it appears that $\alpha_e(\text{NO}^+)$ varies as about $T^{-0.9}$ within the temperature range 200 K $\leq T \leq 600$ K and also $\alpha_e(\text{NO}^+)$ varies as approximately $T_e^{-0.9}$ for T_e up to 2000 K or so. The reasons why the pulsed afterglow $\alpha_e(\text{NO}^+)$ data are not consistent with this are not obvious but may relate to the uncertainties in determining T_e in these plasmas when it exceeds T_+ and T_+ . A $T^{-0.9}$ variation for $\alpha_e(\text{NO}^+)$ is greater than that for O_2^+ and NH_4^+ and might indicate a greater involvement of the indirect recombination mechanism in this reaction.

4. Conclusions

The accumulated data for $\alpha_e(\text{O}_2^+)$ are in close accord in magnitude and are consistent with a variation proportional to $T^{-0.7}$ within the range 200 K $\leq T \leq 600$ K. Most of the available $\alpha_e(\text{O}_2^+)$ data suggest a similar $T_e^{-0.7}$ variation up to $T_e = 5000$ K. It is reasonable to expect that $\alpha_e = \alpha_e$ at low T (or T_e) (≤ 1000 K), where vibrational excitation of the molecular ions is minimal, and thus at these temperatures a common variation proportional to $T^{-0.7}$ is appropriate. Departures from this rather simple situation can, however, be expected at higher temperatures where vibrational excitation becomes significant (see e.g. Bardsley 1983). Data for $\alpha_e(\text{NH}_4^+)$ and $\alpha_e(\text{NH}_4^+)$ are sparse. The present $\alpha_e(\text{NH}_4^+)$ data suggests a variation proportional to $T^{-0.6}$ within the range 300 K $\leq T \leq 600$ K but within error this is indistinguishable from the $T^{-0.5}$ variation theoretically predicted for the direct mechanism of dissociative recombination. The present data for $\alpha_e(\text{NO}^+)$ indicates a variation proportional to $T^{-0.9}$

in the range $200 \text{ K} \leq T \leq 600 \text{ K}$ and the $\alpha_e(\text{NO}^+)$ derived from ionosphere observations indicate a $T_e^{-0.85}$ variation within the range $600 \text{ K} \leq T_e \leq 2500 \text{ K}$. The present $\alpha_i(\text{NO}^+)$ values and the $\alpha_e(\text{NO}^+)$ values derived from the ionospheric data and from the ion trap and merged beam $\sigma_E(\text{NO}^+)$ data converge towards common values above 600 K. Significant differences are apparent between the measured $\alpha_i(\text{NO}^+)$ and the derived $\alpha_e(\text{NO}^+)$ at lower temperatures; these differences are probably due to difficulties in accurately establishing the centre-of-mass electron energies at very low energies (see e.g. the data given in Mul and McGowan 1979 and Froelich *et al* 1983), and the associated uncertainties in determining σ_E at these very low energies. Whilst σ_E values are clearly more fundamental parameters than α_i or α_e values, the latter parameters are of greater practical value in de-ionisation rate calculations in plasmas such as the ionosphere (which is the rational for many of these measurements). An important conclusion to be drawn from the data presented in this paper is that it is preferable to measure α_i and α_e directly when this is practicable. Unfortunately this is not always possible and, even when it is, then the range of temperatures over which such studies can be carried out is rather limited. Then it is necessary to derive α_e from σ_E data. However, as the data of figure 5 illustrate, this procedure has limitations in that the values of α_e derived at low temperatures using this procedure are subject to appreciable errors.

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APPENDIX 2

ATTACHMENT COEFFICIENTS FOR THE REACTIONS

OF ELECTRONS WITH CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 ,

Cl_2 AND SF_6 DETERMINED BETWEEN

200 K and 600 K USING THE FALP TECHNIQUE

J.Phys B: At.Mol.Phys. 1984 (in press)

Attachment Coefficients for the Reactions of Electrons
with CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 Determined
between 200 and 600K Using the FALP Technique

by

D. Smith, N.G. Adams and E. Alge

Department of Space Research

University of Birmingham

Birmingham B15 2TT

England

Short Title: Electron Attachment to CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 ,
 Cl_2 and SF_6

Physics Abstracts Classification Number: 34.00

Abstract

The rate coefficients, β , for the attachment reactions of electrons with CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 have been measured under truly thermal conditions over the approximate temperature range 200-600K using a flowing afterglow/Langmuir probe apparatus. The β values obtained at 300K are 3.9×10^{-7} , 2.6×10^{-7} , 3.2×10^{-9} , 4.4×10^{-9} , 2.0×10^{-9} and $3.1 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$ respectively. From the variation with temperature of β for the CCl_2F_2 , CHCl_3 and Cl_2 dissociative attachment reactions, activation energies, E_a , of 0.15eV, 0.12eV and 0.05eV respectively were derived. The β for CCl_4 , CCl_3F and SF_6 are close to their theoretical limiting values within the temperature range investigated. While Cl^- was the only product ion observed for the reactions involving chlorine-containing molecules, both SF_6^- and SF_5^- were observed for the SF_6 reaction. The data obtained are compared with previous data and the separate influences of electron temperature and gas temperature are noted.

1. Introduction

Electron attachment studies are of fundamental importance to the understanding of electron-molecule interactions and the mechanism of negative ion formation (see eg. Massey 1976) and are of practical value for example in the design of efficient gas lasers (Chantry 1982) and in the choice of insulation suitable for high voltage devices (Christophorou et al 1982). The objective of the work described in this paper was to measure the rate coefficients, β , for the attachment reactions of thermalised electrons with several molecular gases at temperatures in the approximate range 200-600K using our flowing afterglow/Langmuir probe (FALP) apparatus. Using the FALP, the rate coefficients for several types of plasma reactions have already been determined under truly thermal conditions, including positive ion/negative ion recombination (Smith and Church 1976, Smith and Adams 1983) and electron/ion recombination (Alge et al 1983).

Electron attachment has been studied in numerous laboratories using a variety of techniques. Much of the early work (prior to 1976) has been summarised in the books by Massey (1976) and by Christophorou (1971) and many other excellent papers on this topic have been published in the last few years. Some of these papers and the results therein will be referred to in relation to the present work in Section 3. The gases chosen for the present study were CCl_4 , CCl_3F , CCl_2F_2 , CHCl_3 , Cl_2 and SF_6 for which previous data indicate the electron attachment rate coefficients, β , to be relatively large at room temperature. The precise values of β at room temperature and how the β values vary with temperature are not well established and this was a major motivation for the study.

2. Experimental

2.1. Apparatus

The FALP apparatus has been discussed in detail previously in relation to studies of ionic and electronic recombination (Smith and Church 1976, Alge et al 1983). A schematic of the apparatus is given in Fig. 1. In brief, the principle of operation is as follows. Flowing afterglow plasmas are created in a tube (~100cm long and ~8cm diameter) by a microwave discharge through a fast flowing carrier gas (helium in the present studies at pressures between 0.5 and 1 Torr). Hence a thermalised afterglow is distributed along the length of the flow tube. By introducing controlled quantities of appropriate gases into the afterglow via one of two "ring ports" located at different positions along the flow tube (see Fig. 1a), various ionic and electronic reactions can be studied under truly thermalised conditions (Dean et al 1974).

The ring ports are shown schematically in Fig. 1a. The attaching gas was introduced against the carrier gas flow in order to ensure the rapid dispersion of the electron attaching gases across the diametric plane of the flow tube, thus minimising the mixing distance (ϵ). Temperature variation over the approximate range 80K to 600K is achieved by heating or cooling the complete flow tube. The essential plasma diagnostic is a small cylindrical Langmuir probe which can be positioned at any point on the axis of the flow tube (the z-coordinate). With it, the electron, positive ion and negative ion number densities (n_e , n_+ and n_- respectively) can be determined with a spatial resolution of about 1mm. The probe technique has been discussed in detail in previous papers (Smith and Goodall 1968, Smith and Plumb 1972). A pinhole orifice/differentially pumped mass spectrometer/detection system is located at the downstream end of the flow tube to determine the positive and negative ion composition

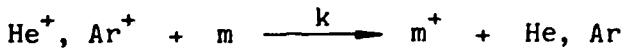
of the afterglow plasmas. By measuring the axial gradients of n_e , n_+ and n_- as appropriate, and also the plasma flow velocity, v_p , (typically $\sim 10^4 \text{ cms}^{-1}$, Adams et-al 1975) the rate coefficients for a wide variety of reactions can be determined.

2.2. Procedure

In the present experiments, appropriate quantities of the electron attaching gases were added into helium afterglow plasmas into which a sufficient amount of argon (equivalent to a pressure of a few millitorr) had been added upstream in order to destroy all $\text{He}(2^1S)$ and $\text{He}(2^3S)$ metastable atoms. When present these metastable atoms react with the electron attaching gas resulting in the production of electrons in the afterglow. n_e was measured with the probe both upstream and downstream of the attaching gas entry port. In the upstream region, the loss of electrons is via ambipolar diffusion predominantly with Ar^+ (and some He^+) and the ambipolar diffusion coefficient for the electrons, D_{ae} , is readily determined from the n_e versus z data. In the downstream region, electron attachment occurs in addition to ambipolar diffusion resulting in a greatly increased loss rate of electrons. Analysis of the n_e versus z data provides a value for the electron attachment rate coefficient, β .

In these experiments it is essential to be cognisant of the following important processes which if not properly accounted for may result in erroneous β values.

(a) Molecular positive ions, m^+ , are inevitably generated to some degree due to ion-molecule reactions (rate coefficient k) between the atomic ions Ar^+ and He^+ and the electron attaching gas, m , thus:



Then the relatively rapid process of dissociative recombination of m^+ with electrons (Bardsley and Biondi 1970) can enhance the rate of loss of n_e , unless n_e and/or n_{m^+} (the molecular positive ion number density) are sufficiently small that recombination loss is insignificant. Specifically, the loss rate of electrons via dissociative recombination, $\propto n_e n_{m^+}$, must be much less than the loss rate of electrons via attachment, $\beta n_e n_m$, (\propto is the dissociative recombination coefficient and n_m is the number density of the electron attaching gas, m). If this condition is not satisfied, then the decrease of n_e is influenced by the production rate of m^+ (i.e. $k n_m n_{\text{Ar}^+}$) and when $\propto n_e n_{m^+} > k n_m n_{\text{Ar}^+}$ then the n_e versus z data provide a value for k . The values of k determined in this way are in acceptable agreement with the values determined in associated selected ion flow tube (SIFT) experiments (see Section 3 and Table 2). In principle, such problems can be eliminated by performing the experiments at sufficiently low n_e , but unfortunately the probe technique did not allow accurate measurement of n_e much below 10^8 cm^{-3} . Consequently we were unable to accurately measure β values smaller than about $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Very recently, the probe technique has been refined to allow measurement of n_e as low as 10^7 cm^{-3} , thus lowering the limiting measurable value of β to about $10^{-10} \text{ cm}^3 \text{ s}^{-1}$.

(b) When studying the most rapid attachment reactions (e.g. the SF_6 and CCl_4 reactions), the number density of the attaching gas, n_m , must necessarily be very small otherwise n_e reduces to rapidly with z (i.e. $\partial n_e / \partial z$ is too large to allow sufficiently accurate n_e versus z measurements to be made). However, n_m must always be appreciably greater than n_e , otherwise the reduction in n_m due to the attachment process results in an

axial gradient in n_m . This would greatly complicate the interpretation of the n_e versus z data usually resulting in erroneously small β values. This effect was investigated by measuring " β " for different initial values of n_e and from these studies we were able to determine initial values of n_e for which accurate β determinations could be made (i.e. for which β is independent of n_e).

Of the gases used in this study, the CCl_2F_2 and Cl_2 were taken directly from cylinders and passed via a flow measuring system into the afterglow. However, the very large β for the SF_6 , CCl_4 and CCl_3F reactions necessitated that these gases were "diluted" with helium to facilitate accurate measurements of the flow rates into the afterglow. Since $CHCl_3$ is a liquid, it was also necessary to use a mixture of its vapour with He. Mixtures typically consisted of 0.1% to 1% of the attaching gases. Experiments were carried out with mixtures of different relative concentrations to check for consistency in preparation and calibration.

2.3 Data Analysis

Suitable plasma conditions have been established such that electron loss in the reaction zone was due only to ambipolar diffusion and attachment. The appropriate continuity equation for n_e is then:

$$\frac{v_p}{p} \frac{\partial n_e}{\partial z} = D_{ae} \nabla^2 n_e - \beta n_e n_m \quad (1)$$

This equation cannot be solved analytically to give $n_e(z)$ since D_{ae} is a function of n_-/n_e (i.e. $D_{ae} \approx 2D_+ (1 + n_-/n_e)$; D_+ is the free diffusion coefficient appropriate to the positive ions present in the plasma). Oskam (1958) and Biondi (1958) have indicated how $n_e(z)$ can be obtained from

equation (1) when negative ion formation is occurring. Their approach is to solve the appropriate continuity equations for $n_+(z)$ and $n_-(z)$ and hence obtain $n_e(z)$ using the quasineutrality condition $n_e(z) + n_-(z) = n_+(z)$. Expressions for both $n_+(z)$ and $n_-(z)$ are readily obtained if it is assumed that (i) n_+ reduces by diffusion only, (ii) diffusive loss of n_+ occurs only via the fundamental mode and (iii) there are no volume loss processes for negative ions (i.e. no negative ion diffusion or recombination). Under these circumstances:

$$n_e(z) = \frac{n_e(0)}{1 - \nu_D/\nu_a} \left[\exp \left(-\frac{\nu_a z}{v_p} \right) - \frac{\nu_D}{\nu_a} \exp \left(-\frac{\nu_D z}{v_p} \right) \right] \quad (2)$$

where $\nu_D = D_{ae}/\Lambda^2$, $\nu_a = n_m \beta$ and Λ is the characteristic diffusion length of the flow tube. As discussed in Section 2.2, condition (i) can be satisfied in our experiment by controlling n_e and hence eliminating positive ion-electron recombination. Condition (ii) is met by taking measurements sufficiently far downstream such that higher order diffusion modes have decayed (Smith et al. 1975, Adams et al. 1975). Condition (iii) is satisfied since even for large ratios of n_-/n_e , the ambipolar space charge field in the plasma inhibits diffusive loss of negative ions (Oskam 1958), and since it can readily be shown from our previous detailed studies of positive ion-negative ion recombination that at small n_+ and n_- ionic recombination loss is negligible. As can be seen from equation (2), the simplest situation from the data analysis viewpoint would be to obtain data under conditions such that $\nu_D \ll \nu_a$ (whence equation (2) reduces to $n_e(z) = n_e(0) \exp(-\nu_a z/v_p)$). In practice this could not usually be achieved (especially at 455 and 590K) and so the data was analysed according to equation (2) by curve fitting using measured values for the parameters ν_D , n_m and v_p . ν_D was determined in the upstream part of the afterglow or in the absence of the attaching gas (see Figs. 1 and 2). Equation (2) predicts that the $\ln n_e$ versus z curve (see Fig. 2) will have an increasing

slope with increasing z (that is, as n_-/n_e increases) becoming very steep for $n_-/n_e \gg 1$ when the ambipolar field collapses allowing rapid free diffusion of the remaining electrons to occur (this transition to free diffusion is not described by equation (2)). Thus a rapid transition occurs from an electron dominated plasma to a negative ion dominated plasma devoid of electrons (see Fig. 1b). When this transition can be initiated at sufficiently high n_+ , n_- , then positive ion-negative ion recombination can be studied (Smith and Church 1976).

3. Results and Discussion

3.1 General Comments

The summarised values of β obtained from this study are given in Table 1 together with some previous values of β determined at 300K using other techniques. Note that only upper limit values are given for the three slowest reactions at 200K, these being close to the rate coefficients for the ion-molecule reactions of the attaching gases, m , with Ar^+ (the dominant positive ion in the plasma prior to the introduction of the attaching gas). The reason for adopting these limiting values is clear from the discussions given in Section 2.2. The rate coefficients for the $\text{Ar}^+ + m$ reactions were accurately determined at 300K using our selected ion flow tube (SIFT) apparatus which has been described in detail elsewhere (Smith and Adams, 1979). These rate coefficients are listed in Table 2 which also includes rate coefficients for several other gases which were originally included in this attachment study but for which the β values were found to be too small to be measured by the present technique. The rate coefficients for all these $\text{Ar}^+ + m$ reactions are essentially equal to their respective ion-molecule collisional limiting values, ($\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$;

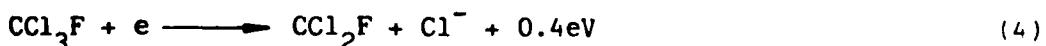
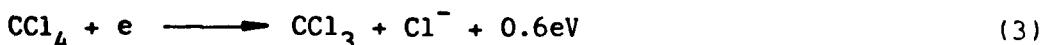
Su and Bowers 1973), and so they are expected to be sensibly independent of temperature (Ferguson 1972, Adams and Smith 1983).

Sources of error in the determination of β by the FALP technique are as follows. Only relative values of n_e are required for these experiments and these can be determined quite accurately ($\sim 2\%$). (Absolute values of n_e can be determined to about 10%, most of this error being due to uncertainty in the surface area of the Langmuir probe). The plasma flow velocity, v_p , and the attaching gas number density are both uncertain by about 5%. The temperature in the reaction zone is also subject to a small uncertainty (a maximum of 2% at all temperatures). The largest single source of error relates to the fitting of the n_e vs z curves, examples of which are given in Fig. 2, including one curve for the pure diffusion case from which v_D is obtained, and two curves relating to different values of n_m from which the v_a values and thus the β values are derived. The total estimated error in the β values is $\pm 15\%$ at 205 and 300K and somewhat larger ($\pm 20\%$) at 455 and 590K due to the greater importance of diffusive loss relative to attachment loss.

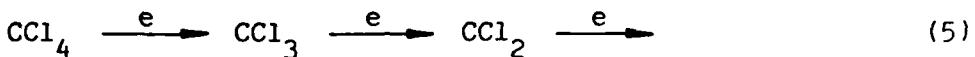
3.2 Comments on the Individual Reactions

3.2.1 CCl_4 and CCl_3F :

Dissociative attachment is so fast that only very small number densities of the reactant gases (n_m) were needed in the afterglow. Indeed, the required n_m were so small that positive ion reactions did not occur to any extent. This therefore ensured that molecular positive ions were not produced and thus electronic and ionic recombination did not affect the n_e loss rate. In both reactions, only Cl^- ions were observed as products:



The energies released in these reactions and the other reactions discussed in this paper are approximate and are derived from data taken from various papers (Wentworth et al. 1969, Fehsenfeld 1970, Schultes et al. 1975, Dispert and Lacmann 1978, Schumacher et al. 1978). Production of F^- in reaction (4) is $\sim 2\text{eV}$ endoergic and consequently none was observed in these thermal energy experiments. We speculate that sequential reactions of this kind:



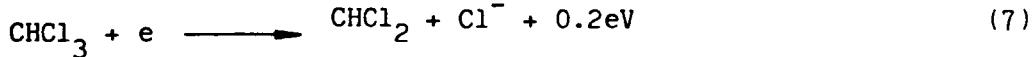
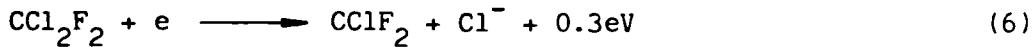
could be occurring but we could not verify this because the product ion in each case is Cl^- . Although the second reaction stage of (5) can be shown to be exoergic this in itself is no guarantee of an appreciable β value for the reaction.

Table 1 indicates that our $\beta(\text{CCl}_4)$ and $\beta(\text{CCl}_3\text{F})$ values at 300K are in good agreement with recent values obtained by other workers. A small decrease of $\beta(\text{CCl}_4)$ with temperature has been observed previously (Warman and Sauer 1971) and a slow decrease in $\beta(\text{CCl}_4)$ with increasing temperature is also discernible in the present data. Conversely, $\beta(\text{CCl}_3\text{F})$ slowly but definitely increases from a value about half that for $\beta(\text{CCl}_4)$ at 205K to a maximum value which, within error, is equal to the value for $\beta(\text{CCl}_4)$ at 455K. This is consistent with a small activation energy barrier, E_a , in the CCl_3F reaction as indicated by the previous data of Wentworth et al. (1969). An estimate of the magnitude of E_a (CCl_3F) can be obtained from the slope of an Arrhenius plot giving E_a (CCl_3F) $\approx 0.02\text{eV}$ ($\approx 2 \text{ kJ mole}^{-1}$). The nature of activation energy barriers in these attachment reactions has been discussed in several papers (Wentworth et al. 1967, Wentworth et al. 1969, Christodoulides et al. 1975). No activation energy barrier exists in the CCl_4 reaction. The very large value for $\beta(\text{CCl}_4)$ of

$3.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300K is close to β_{\max} , the theoretical maximum for electron attachment where $\beta_{\max} \approx 5 \times 10^{-7} (300/T)^{\frac{1}{2}} \text{ cm}^3 \text{ s}^{-1}$. This result is derived from the theoretical maximum cross section for the process which is formulated in terms of the electron de Broglie wavelength (Warman and Sauer 1971). At 455K, $\beta(\text{CCl}_3\text{F})$ also has apparently reached its upper limit value and thus both it and $\beta(\text{CCl}_4)$ can only decrease at higher temperatures. A more sophisticated theoretical treatment by Klots (1976) assumes that the interaction is dominated by the polarization potential and the process is purely s-wave capture. This approach yields a value for $\beta(\text{CCl}_4)$ of $3.29 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at room temperature. The weak negative temperature variation of $\beta(\text{CCl}_4)$ is presumably a reflection of the weak electron energy dependence predicted by Klots's approach (West et al. 1976, Foltz et al. 1977).

3.2.2 CCl_2F_2 and CHCl_3 :

These reactions are similar to each other in that appreciable activation energy barriers exist for both as is manifest by the large increase in the β values with temperature (Table 1). Again Cl^- is the only observed product ion in both reactions:



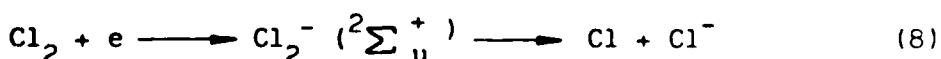
At 205K these reactions are too slow to allow an accurate determination of β . The previous values at 300K for both $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$ are quite varied (see Table 1) but it is clear that the present values are somewhat larger than the majority. We have no explanation for this. From the present data, values of E_a for both reactions have been obtained from the slopes of the Arrhenius plots shown in Fig. 3. Thus $E_a(\text{CCl}_2\text{F}_2) \approx 0.15\text{eV}$ ($\approx 15 \text{ kJ mole}^{-1}$) and $E_a(\text{CHCl}_3) \approx 0.12\text{eV}$ ($\approx 12 \text{ kJ mole}^{-1}$) which are in good agreement in both cases with the previous values derived using different techniques. The previous values in kJ mole^{-1} are: CCl_2F_2 : 19 (electron

Chen and Chantry 1972) 15 (pulse sampling; Wentworth et al. 1969); CHCl_3 : 10 (ECR; Schultes et al. 1975), 9 (microwave; Warman and Sauer 1971), 13 (pulse sampling; Wentworth et al. 1967). That there is good agreement between the E_a values determined using these different techniques whereas there are significant differences in the absolute values of β implies that systematic errors are involved in one or all the experiments. Such could for example be due to the determination of the partial pressures of the attaching gases. At the highest temperature of the present experiments $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$ are both approaching an order-of-magnitude smaller than β_{\max} . Presumably β_{\max} for these reactions would be approached at sufficiently high temperatures such that the E_a do not impede the reactions.

3.2.3 Cl_2 :

The present $\beta(\text{Cl}_2)$ values are again represented by an Arrhenius plot in Fig. 3. A relatively small increase in $\beta(\text{Cl}_2)$ with temperature is indicated leading to a derived activation energy $E_a(\text{Cl}_2) \approx 0.05\text{eV}$ ($\approx 5\text{ kJ mole}^{-1}$). Again it is perhaps significant that this $E_a(\text{Cl}_2)$ is in good agreement with the ECR value of Christodoulides et al. (1975) ($\text{also } 5\text{ kJ mole}^{-1}$) but the magnitudes of the corresponding ECR values of $\beta(\text{Cl}_2)$ are smaller by about a factor 7. However other ECR data of Schultes et al. (1975) from the same laboratory indicates a $\beta(\text{Cl}_2)$ at 300K only a factor 2 smaller than the present value. Flowing afterglow data due to Sides et al. (1976) indicate that $\beta(\text{Cl}_2) = (3.7 \pm 1.7) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 350K which is in closer agreement with the present value.

A discussion of the mechanism of this reaction is given by Christodoulides et al. (1975) where it is concluded that the dissociative attachment reaction at thermal energies proceeds via the intermediate temporary negative ion $\text{Cl}_2^- ({}^2\Sigma_u^+)$ thus:



Kurepa et al. (1981) have considered several possible intermediate Cl_2 states and have calculated $\beta(\text{Cl}_2)$ over a wide range of mean electron energies using their measured cross section data. Their calculated values are quite consistent with the present value obtained at 300K. Significantly their calculations show little change of $\beta(\text{Cl}_2)$ as a function of the mean electron energy in the thermal energy regime. Thus it appears that the observed increase of $\beta(\text{Cl}_2)$ with temperature in our experiments is mainly due to the internal excitation of Cl_2 at higher temperatures.

3.2.4 SF_6 :

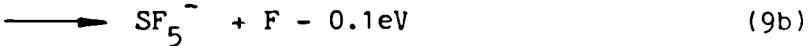
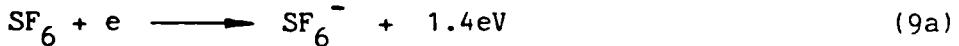
A good deal of effort has been devoted to the determination of the rate coefficients and cross sections for electron attachment to SF_6 . The present and some previous values for $\beta(\text{SF}_6)$ are given in Table 1. Most of the previous values of $\beta(\text{SF}_6)$ lie within the range $(2-3) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ with one set indicating values of $(2.2 \pm 0.2) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and another set indicating values of $(2.8 \pm 0.3) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. The highest reported value of $3.9 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ was obtained using the pulse sampling technique (Ayala et al. 1981b, from reanalysis of previous data), although using the same technique under different conditions, values of 2.8 and $0.54 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ were also obtained. The present 300K value for $\beta(\text{SF}_6)$ of $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ supports the previous higher values and agrees with the pulsed afterglow value of Mahan and Young (1966) of $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ *. Clearly the present measurements cannot be reconciled with the set of measurements close to $2.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ which includes the recent value due to Crompton and Haddad (1983). This set also includes the flowing afterglow value of Fehsenfeld (1970) who also measured $\beta(\text{SF}_6)$ between 293K and 523K and concluded that, within the scatter of his data, no temperature variation of $\beta(\text{SF}_6)$ could be discerned. However, within the present data there is

* Fessenden and Bansal (1970) state that this value was incorrectly reported and that the correct value is $2.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$.

an indication of a peak in $\beta(\text{SF}_6)$ within the 400-500K temperature range which is more evident if only the SF_6^- channel is considered (β for SF_6^- production at 590K is $\sim 3.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, see below). This may be a manifestation of the peak in the attachment cross section for SF_6^- production at very low electron energies (McCorkle et al. 1980)

It is worthy of note that electron transfer from high Rydberg states of atoms to electron attaching molecules has been demonstrated to be consistent with an "essentially free" electron model (Dunning and Stebbings 1982). Rate coefficients of $\sim 4 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ have been derived for the process of electron transfer from Xe Rydberg atoms to SF_6 (referring to mean electron energies below 20meV) by Foltz et al. (1977) which tends to support the higher values for $\beta(\text{SF}_6)$ derived in the present experiments. The theory of Klots (1976) yields a value for $\beta(\text{SF}_6)$ of $2.61 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at room temperature. However, it is interesting to note that the ratio of the present experimental values of $\beta(\text{CCl}_4)$ to $\beta(\text{SF}_6)$ at 300K is identical to the ratio of the room temperature values calculated by Klots (1976).

The SF_6 reaction is unique in the present series of reactions in that both dissociative and nondissociative attachment occurs:



Fehsenfeld (1970) observed that the fraction of the SF_5^- product increased with increasing temperature according to an Arrhenius-type law, and deduced a value of $E_a = 0.43\text{eV} (\equiv 43 \text{ kJ mole}^{-1})$ for reaction (9b). Compatible results were obtained in the present experiments, the ratio $\text{SF}_5^-/\text{SF}_6^-$ being $\sim 5 \times 10^{-3}$ at 300K, $\sim 7 \times 10^{-2}$ at 455K and ~ 0.25 at 590K. Again, therefore, it appears that systematic errors are involved in either the present and/or Fehsenfeld's experiments which do not lead to serious differences in derived E_a values (determined from $\text{SF}_5^-/\text{SF}_6^-$ ratios) but do result in significant differences in the absolute values of $\beta(\text{SF}_6)$.

4. Conclusions

The afterglow plasma is an ideal medium in which to determine electron attachment reaction rate coefficients under truly thermal conditions and over appreciable temperature ranges. In this study we have measured attachment rate coefficients, β , for several gases. For the very fast reactions, for which the β only vary slowly with temperature and which are essentially at their theoretical maximum values (e.g. those for the CCl_4 and CCl_3F reactions), our data is in good agreement with previous data. For the slower reactions (i.e. CHCl_3 , CCl_2F_2 and Cl_2) for which the β vary exponentially with temperature, our β values appear to be somewhat larger than previous values and yet the activation energies derived from our data for these reactions are in good agreement with previous values. Systematic errors in the present or the previous experiments could explain such differences. It appears from the present data that a maximum occurs in $\beta(\text{SF}_6)$ in the 400-500K range. Since it is known that there is a maximum in the cross section for low energy electron attachment collisions with SF_6 , we presume that this is a contributing factor to the maximum observed in $\beta(\text{SF}_6)$. Clearly however the temperature dependence of the thermal rate coefficients are a convolution of the variations of the cross sections with both electron energy and with the temperature of the attaching gas (the rotational and vibrational states), folded with the Maxwellian distribution of the electron energies in the thermalised plasma. Often an increasing electron energy results in decreasing β (Christophorou et al. 1971, McCorkle et al. 1980) whereas an increase in internal excitation of the attaching molecules usually results in an increase in β as activation energy barriers are overcome. The latter phenomenon is manifest by the present data for $\beta(\text{CCl}_2\text{F}_2)$ and $\beta(\text{CHCl}_3)$. Thus it is clear that temperature dependence studies of β can provide fundamental information on electron/molecule interactions and interaction potentials.

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Phys. Rev. Lett. 36 854.

Table Captions

Table 1 Summary of the electron attachment coefficients, β , obtained in the present study at 205, 300, 455 and 590K. The total estimated error is \pm 15% at 205 and 300K and \pm 20% at 455 and 590K. Some values of β obtained at 300K by other workers using the techniques indicated are also listed.

Table 2 Rate coefficients measured at room temperature (297K) in a SIFT apparatus for the reactions of Ar^+ with the molecules indicated. Also given are the major product ions in order of their importance in the product spectrum.

Table 1

Molecule	Present results				Previous results, obtained at 300K using the techniques indicated below	Electron Attachment Coefficients β ($\text{cm}^3 \text{s}^{-1}$)
	205K	300K	455K	590K		
CCl ₄	4.1	3.9	3.7	3.5	$\times 10^{-7}$ 4.1 ^a , 4.1 ^b , 4.0 ^c , 3.55 ^d , 2.9 ^e , 2.9 ^f , 1.5 ^g , 4.4, 1.3 ^h	(4.2, 1.6,
CCl ₃ F	2.2	2.6	3.6	3.3	$\times 10^{-7}$ 1.0 ⁱ , 1.3 ^j , 1.2 ^e , 1.0 ^k , 2.43 ^l , 2.37 ^m	
CCl ₂ F ₂	<1	3.2	16	53	$\times 10^{-9}$ 0.7 ⁱ , 5.9 ⁿ , 1.7 ^j , 1.36 ^o , 1.2 ^k , ~1 ^p , 0.6 ^q , 0.4 ^g	
CHCl ₃	<1	4.4	17	36	$\times 10^{-9}$ (2.6 ^h , 2.2) ^r , (2.2-2.6) ^b , 4.9 ^g , 3.8 ^e , (3.8, 2.66, 2.3, 2.0) ^l	
Cl ₂	<1	2.0	3.3	4.8	$\times 10^{-9}$ 0.31 ^s , 1.2 ^r , 3.7 ^t , 0.28 ^z	
SF ₆	3.1	3.1	4.5	4.0	$\times 10^{-7}$ (3.9 ^y , 2.8, 0.54) ^h , 2.6 ^a , 3.1 ^u , (2.7, 2.8) ^v , 2.21 ^w , 2.0 ^x , 2.21 ^y , 2.28 ^m	

^a Mothes and Schindler (1971); ECR
^b Warman and Sauer (1971); microwave
^c Warman and Sauer (1970); microwave
^d Davis et al. (1973); drift-dwell-drift
^e Blaunstein and Christophorou (1968); swarm
^f Bouby et al. (1965); swarm
^g Lee (1963); swarm
^h Ayala et al. (1981b); pulse sampling
ⁱ Schumacher et al. (1978); ECR
^j Wentworth et al. (1969); pulse sampling
^k Christophorou and Stockdale (1968); swarm
^l McCorkle et al. (1982); swarm
^m Crompton et al. (1982), and Crompton and Haddad (1983); Cavalleri technique
ⁿ Chen and Chantry (1972); beam
^o Bansal and Fessenden (1973); microwave
^p Christophorou et al. (1974); swarm
^q Buchelnikova (1959); total ion current
^r Schultes et al. (1975); ECR
^s Christodoulides et al. (1975); ECR
^t Sides et al. (1976); flowing afterglow at 350K
^u Mahan and Young (1966); stationary afterglow/microwave
^v Christophorou et al. (1971); swarm
^w Fehsenfeld (1970); flowing afterglow
^x Davis and Nelson (1970); swarm
^y Fessenden and Bansal (1970); microwave
^z Ayala et al. (1981a); pulse sampling

Table 2

Reactant molecule	Major product ions	Rate coefficient (cm ³ s ⁻¹)
CCl ₄	CCl ₃ ⁺ , CCl ₂ ⁺	8.1 x 10 ⁻¹⁰
CCl ₃ F	CCl ₂ F ⁺ , CCl ₃ ⁺	8.7 x 10 ⁻¹⁰
CCl ₂ F ₂	CClF ₂ ⁺ , CCl ₂ F ⁺	1.1 x 10 ⁻⁹
CClF ₃	CF ₃ ⁺ , CClF ₂ ⁺	8.7 x 10 ⁻¹⁰
CF ₄	CF ₃ ⁺	6.4 x 10 ⁻¹⁰
CHCl ₃	CCl ⁺ , CHCl ⁺	1.4 x 10 ⁻⁹
CH ₂ Cl ₂	CH ₂ Cl ⁺	1.7 x 10 ⁻⁹
CH ₃ Cl	CH ₃ ⁺ , CH ₂ Cl ⁺	2.0 x 10 ⁻⁹
Cl ₂	Cl ⁺ (80%), Cl ₂ ⁺ (20%)	5.6 x 10 ⁻¹⁰
SF ₆	SF ₅ ⁺	9.6 x 10 ⁻¹⁰
NF ₃	NF ₂ ⁺	9.5 x 10 ⁻¹⁰

Figure Captions

Fig. 1 a) Schematic representation of the FALP experiment including diagnostic instruments, ionization source, gas inlet ports etc.

b) Typical variations of n_e , n_+ and n_- along the flow tube during electron attachment studies.

Fig. 2 Electron density (n_e) profiles obtained at a helium pressure of 0.6 Torr and a temperature of 205K. \circ No electron attaching gas is present; n_e decreases due to ambipolar diffusion only. In the presence of CCl_3F electron attachment increases the rate of loss of n_e : \bullet $n(CCl_3F) = 9 \times 10^8 \text{ cm}^{-3}$, \blacksquare $n(CCl_3F) = 1.6 \times 10^9 \text{ cm}^{-3}$. The transition to an ion-ion plasma is evident at positions of 30 cm and 40 cm respectively.

Fig. 3 Arrhenius plots for the attachment reactions of electrons with CCl_2F_2 (\bullet), $CHCl_3$ (\blacksquare) and Cl_2 (\blacktriangle). The derived activation energies, E_a , are as indicated.

Figure 1.

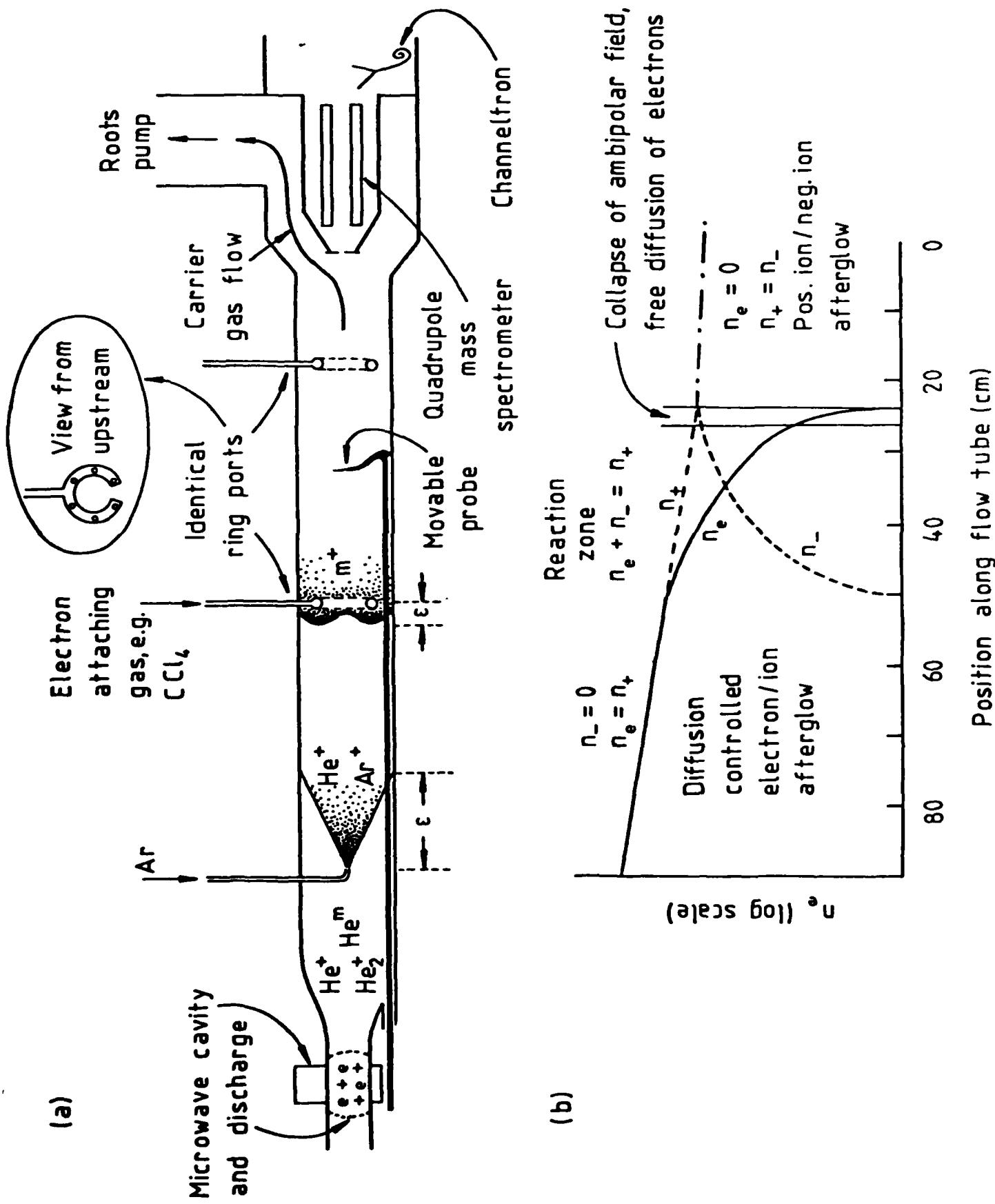


Figure 2.

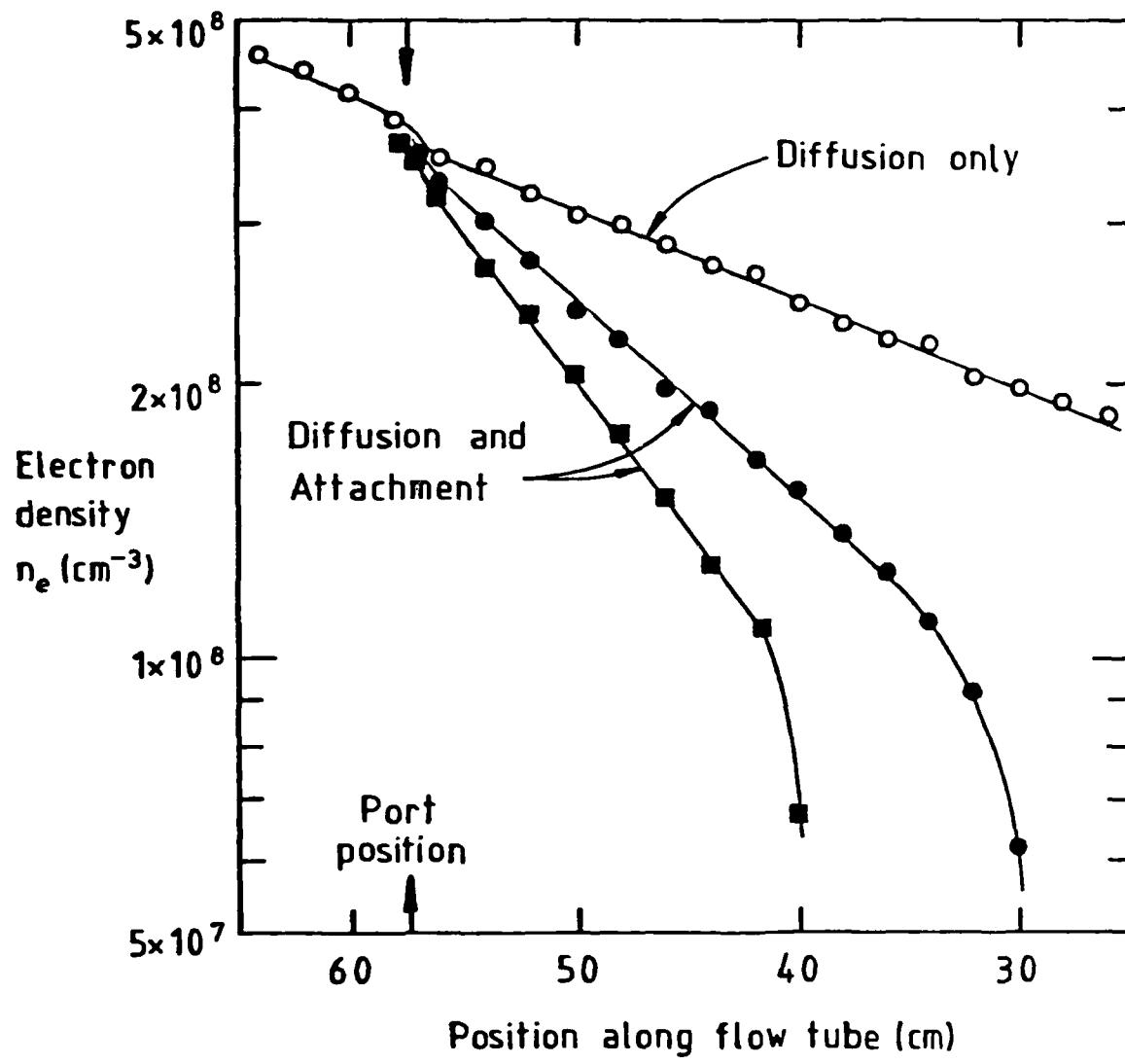
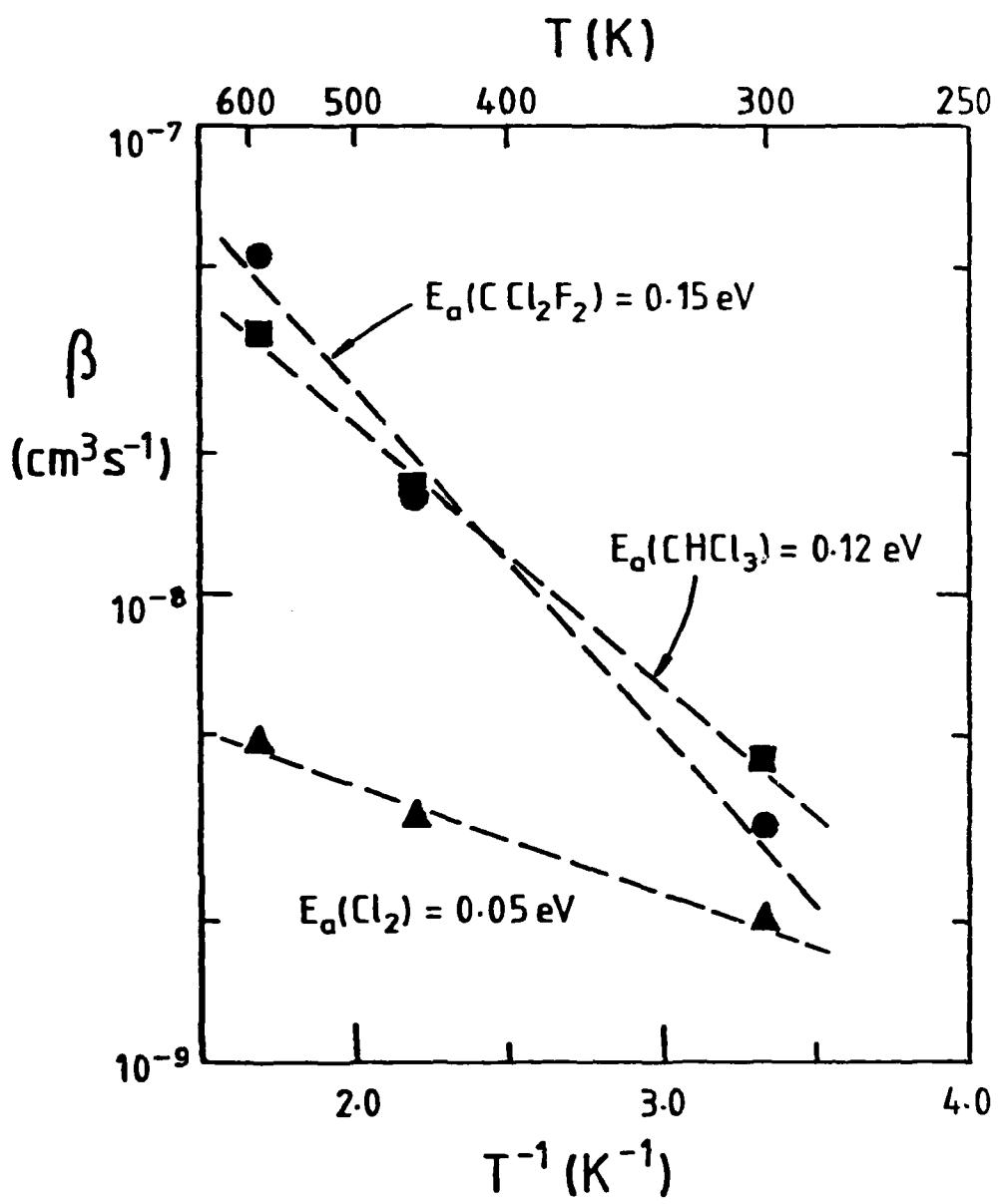


Figure 3.



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